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EVALUATION OF PYRRONES AS MEMBRANES

by H. Scott and F. L. Serafin

Prepared by

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16. Abstract <p>The facile absorption of water by polyimidazopyrrolones (Pyrrolones) suggested a feasibility study to use films of the polymers as membranes for the purification of water by reverse osmosis. This report describes direct osmosis measurements of water, salt, and urea fluxes through Pyrrole membranes. The data indicate comparable flux values and superior water-to-salt permeabilities of the Pyrrolones relative to symmetric cellulose acetate membranes. Coupled with better mechanical strength and chemical resistance, these results suggest that the successful fabrication of asymmetric Pyrrole membranes could lead to substantial improvements over asymmetric cellulose acetate, from which the best reverse osmosis membranes are currently prepared.</p>					
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EVALUATION OF PYRRONES AS MEMBRANES

By H. Scott and F. L. Serafin
The Franklin Institute Research Laboratories

1. INTRODUCTION

Polyimidazopyrrolone or Pyrrone polymers are a new class of thermally stable and radiation resistant aromatic-heterocyclic polymers developed by investigators at the Langley Research Center of the National Aeronautics and Space Administration (references 1-3). We suggested that Pyrrone membranes may be useful in the purification of water by reverse osmosis. In addition to a high water content (up to 12 wt %), Pyrrones feature greater chemical and mechanical durability than cellulose acetate. Low durability is a principal drawback holding up large scale water purification applications of cellulose acetate membranes which in other respects are generally regarded as the most promising membranes developed to date.

This report describes direct osmosis measurements of water, salt and urea fluxes through Pyrrone membranes and a preliminary evaluation of their applicability as reverse osmosis membranes for the purification of water in spacecraft life support systems. The polymers investigated are shown in Figure 1.

Water fluxes of 1.8-15.8 $\mu\text{g}/\text{cm}^2/\text{sec}$ through 2.5-30 μ thick Pyrrone membranes observed in this study compare favorably with reported values for cellulose acetate membranes obtained under similar conditions (reference 4). Moreover, values of up to 114 obtained for the permselectivity or the A/B ratio of intrinsic water to salt permeabilities (reference 5) of Pyrrone membranes were up to 100 times greater than such ratios calculated from cellulose acetate flux data (reference 4). Assuming A/B = 100 for Pyrrone and a mechanism whereby water and salt are independently transported across a Pyrrone membrane as has been found for cellulose acetate (reference 5), the salt rejection was calculated to reach 99% at an applied pressure of only 1 atm over the osmotic pressure (≈ 20 atm) of a 3 wt. % NaCl solution and 99.99% at 120 atm applied pressure, facilitating higher recoveries of purified water and/or lower required applied pressures than attainable with membranes having lower permselectivity such as a physically analogous symmetric type of cellulose acetate membrane (reference 4). Coupled with greater durability of Pyrrone membranes, these findings indicate Pyrrones may outperform cellulose acetate membranes in water purification by reverse osmosis.

2. EXPERIMENTAL

2.1 Preparation of Materials

Pyromellitic dianhydride. - (PMDA) (Princeton Chemical Research) was sublimed for 6 hours through two layers of fiberglass fabric onto a cold finger in a large laboratory sublimator at 200°C/0.05 mm Hg. Three similar

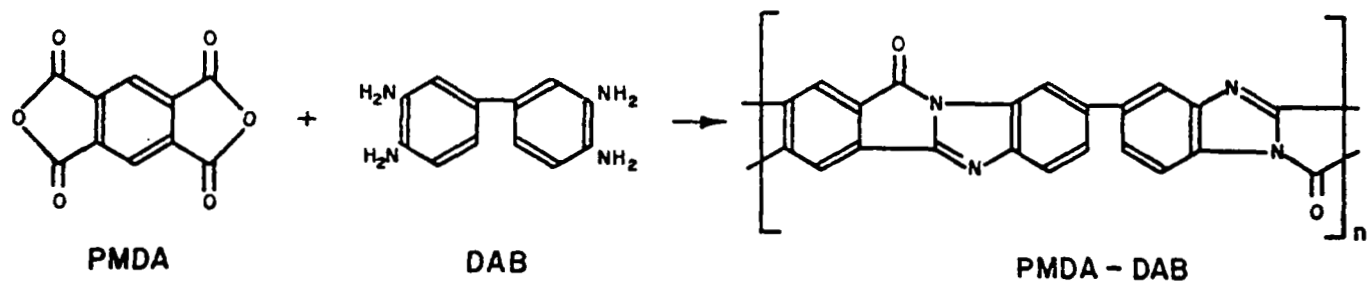
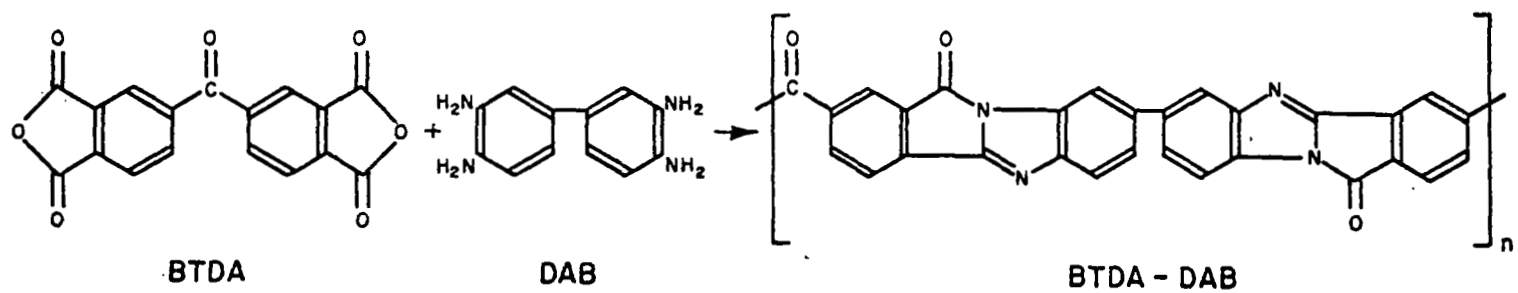


Figure 1. Stepladder Pyrroles

runs yielded 69 g. of colorless sublimate melting at 286-287°C. The yields were about 20-25%. Sublimation by entrainment in a stream of nitrogen was briefly investigated. Higher yields were obtained, but the sublimate had a slightly yellow color.

3,3',4,4' - Benzophenone tetracarboxylic acid dianhydride (BTDA). - (Gulf Chemical Corp.) was similarly sublimed and resublimed at 255°C/0.025 mm Hg. Melting points of products ranged from 221-228°C, apparently depending on exposure to moisture. The larger crystals which fell off the cold finger had the highest melting point when determined immediately following removal from sublimator. Crystalline powder which remained on the cold finger had a lower melting point, as did crushed larger crystals exposed to air for a few minutes.

3,3' - Diaminobenzidine (DAB) (Burdick and Jackson Laboratories, Inc.) was recrystallized from a 2:1 mixture of water and acetonitrile after treatment with charcoal to yield a light tan powder, m.p. 176°C, after vacuum drying for 2 days. A similar recrystallization from water yielded a slightly darker product, m.p. 174-175°C. Recrystallized material was used in all polymerizations.

Dimethylacetamide (E. I. du Pont de Nemours and Co., Inc.), 55 gal. drum quantity, was supplied on special order in 5 gal. drum filled at plant under nitrogen. It was distilled from PMDA for use as solvent in polymerizations.

Polymerization

The procedures were similar to those described by investigators at NASA/Langley (references 1-3). The Pyrrone polymer of BTDA-DAB was prepared by adding 95 ml of a solution of 12.89 g. (0.04 mole) of sublimed BTDA in 100 ml DMAC to a stirred, hot (~ 60°C) solution of 8.56 g. (0.04 mole) of DAB in 100 ml DMAC in a preheated high-speed blender under nitrogen. The blender was wrapped with heating tape. After 30 minutes of stirring, the remainder of the BTDA solution, 0.65 g. in 5 ml DMAC, was added dropwise. Stirring and heating were continued for one hour. Then the polymer dope was centrifuged. The supernatant was decanted off and stored under nitrogen in a dry ice chest. The prepolymer dope had an intrinsic viscosity $[\eta]$ of 1.70 dl/g.

The Pyrrone prepolymer of PMDA-DAB was prepared in a similar manner except that the vessel was not heated. Upon completion of addition of the PMDA solution, stirring at room temperature was continued for about one-half hour, yielding prepolymer solution of intrinsic viscosity $[\eta] = 1.00$.

No excess anhydride was used in either polymer preparation.

Film Casting

Films were cast from prepolymer solutions of intrinsic viscosity $[\eta] > 1$ with an adjustable-clearance film applicator on Pyrex glass plates, 6" X 6" polished on one side to 10 bands. This was done in a filtered laminar air flow work station. After the films were cast, gentle heat was applied beneath the plates from two infrared heating elements. After one hour, the plates

were placed in a forced air oven set at 100°C. The films were cured for various times at 100, 200 and 300°C as noted later in Table 1. After this curing cycle, the films were usually stripped from the glass plate while it was submerged in a water bath to facilitate removal. Film thickness ranged from 2.5-30 microns. Thinner films cast on glass, tin oxide coated glass and Kapton could not be removed under water from substrate without wrinkling or tearing the Pyrrone film.

2.2 Water and Solute Flux Measurements

Water and salt fluxes were measured under direct osmosis conditions using a glass cell as shown in Figure 2. An unsupported 2 cm² membrane was clamped with a neoprene gasket between two half sections of the cell. One side was filled through a Teflon stopcock with 10 ml deionized water and the other side with 10 ml of a solution of 3 wt % solute in deionized water. Both sides were maintained at atmospheric pressure with open attached pipet sections, and were stirred at room temperature by Teflon coated magnetic stirrers placed as close as possible to the membrane. The gasket, stopcock and stirrer assemblies were exhaustively Soxhlet extracted with water prior to use. The volume of water passing through the membrane from the deionized to the salt side of membrane was measured as a function of time. The water volume increase on the salt side was measured periodically by means of a graduated pipet section attached horizontally to the cell. On exceeding pipet capacity, the water flowing out of the pipet was weighed periodically. Salt flux in the opposite direction was measured conductometrically with Pt electrodes on the deionized water side of the cell, using a direct reading conductivity bridge. The readings were converted into actual salt concentrations by reference to a graph of resistance vs. salt concentration constructed from calibration measurements of the conductivity over a wide salt concentration range made in the same cell.

Urea flux was measured by colorimetric assay (reference 6) of periodic increases in urea content on the initially urea-free side of the membrane. However, to increase the urea available for the assay, both compartments of the cell were emptied and replaced by fresh 3 wt. % urea solution and pure water respectively after 1 hour, 2 hours, etc., as indicated in Table 4 giving the flux results.

Most experiments were terminated within six hours; a few were continued up to 72 hours or slightly beyond. In these latter experiments, when the capacity of the pipet on the salt water side was exceeded, the excess water was collected and weighed in a tared receiver. Since initial experiments indicated that water and solute fluxes through PMDA-DAB and BTDA-DAB membranes were similar, and PMDA was more easily purified and polymerized than BTDA, most measurements were made with PMDA-DAB membranes.

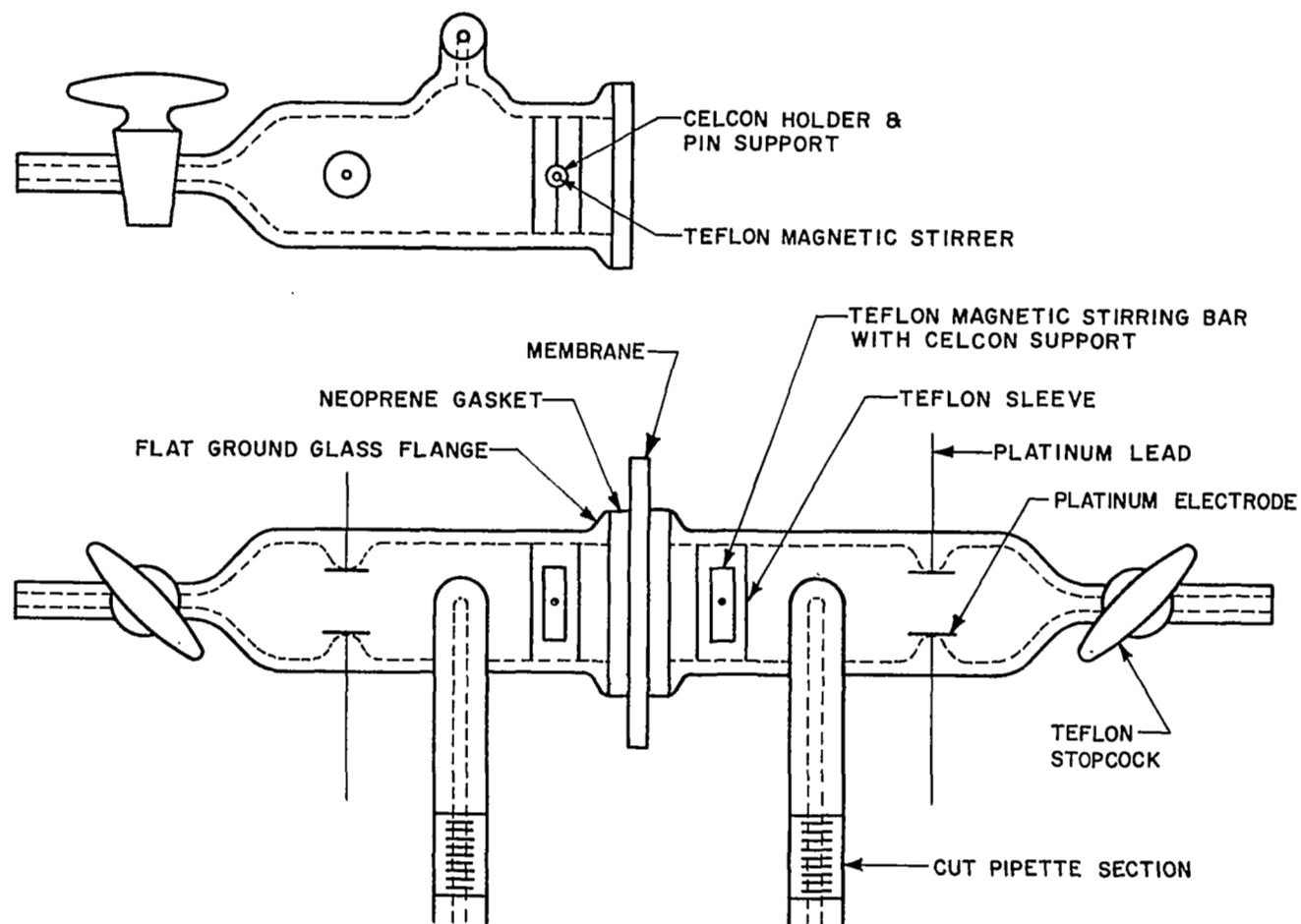


Figure 2. Cell for Measuring Water and Solute Fluxes Through a Membrane

3. RESULTS

First hour water and salt fluxes through PMDA-DAB and BTDA-DAB membranes of increasing thickness are shown in Tables 1-3. Urea flux with time through two PMDA-DAB films and a BTDA-DAB film is given in Table 4. Water and salt fluxes through the same membranes are shown in more detail in Figures 3-14. Indicated salt fluxes are based on measurements of the salt concentration per ml of water on initially ion-free side of the membrane and are uncorrected for water volume contraction due to flow of water to the other side of the membrane. Resulting error is negligible for initial fluxes, but actual salt fluxes at the end of long runs are about 10-20% less than shown.

One membrane was aged in human urine for 30 days at room temperature. Water and salt flux measurements through 11.5 μ film X before and after urine exposure are included in Table 1.

The center area of a PMDA-DAB membrane exposed to urea solution was sometimes noted to become a little lighter in color in the course of a run in comparison with the unchanged dark unexposed outer area held between the half cells. Also, the exposed area became somewhat buckled as if the polymer had extended due to a relaxation or solvation process.

Table 1
First Hour Water and Salt Fluxes and A/B Ratio of Intrinsic Permeabilities^a
Through PMDA-DAB Membranes

Film	Thickness μ	Cure ^b , and Treatment ^c	H ₂ O Flux $\mu\text{g}/\text{cm}^2/\text{sec}$	NaCl Flux $\times 10^3$ $\mu\text{g}/\text{cm}^2/\text{sec}$	A/B ^a
B	2.5	2S	9.7	6.1	1.9
B (1/2 hr)			15.8	3.6	5.4
F	2.5	1S	2.6	2.1	1.5
G	2.5	1S	3.1	2.3	1.6
O	2.5	5S	2.1	4.0	0.6
O (27 hrs)			6.7	5.4	1.5
E	5	2S	6.4	5.3	1.5
J	5	4S	7.2	0.08	110
J (1/2 hr)			6.8	0.17	49
H	8	1S	1.8	5.4	4.1
K	8	1U	2.6	< 0.48	> 6.6
L	8	1S	5.7	2.5	2.8
I	10	3S	5.7	2.8	2.5
M	10	1SS	1.9	1.6	1.5
X	11.5	5S	2.1	0.08	32.01
X (urine aged 30 days)			1.8	13.9	0.158
N	13	5 ^d	7.5	.08	114
N (1/2 hr)			12.0	0.17	86.1
A	30	1U	2.8	.08	42.7

^a See discussion section.

^b Film cure times and temperatures: 1 = 3 hours at 100°C, 2 hours at 200°C, 24 hours at 300°C, 2 = same except 2 hours at 300°C, 3 = same except 3 hours at 300°C, 4 = same except 12 hours at 300°C, 5 - 1/2 hr at 100°C, 1/2 hr at 150°C, 15 hours at 300°C.

^c Film pretreatment: U = untreated, S = soaked overnight in deionized water, SS = soaked overnight in salt (NaCl) solution.

^d Cured 1/2 hour at 100°C, 1/2 hour at 150°C, stripped from glass plate, Soxhlet extracted overnight with water, and cured further 15 hours at 300°C.

Table 2
First Hour Water and Salt Fluxes and A/B Ratio of Intrinsic
Permeabilities^a Through BTDA-DAB Membranes

<u>Film</u>	<u>Thickness μ</u>	<u>Cure^b, and Treatment^c</u>	<u>H₂O Flux μg/cm²/sec</u>	<u>NaCl Flux x 10³ μg/cm²/sec</u>	<u>A/B^a</u>
T	8	S0	3.3	1.6	2.5
R	8	S3	4.1	0.56	8.9
S	10	S6	2.6	0.14	22.6
P	15	U	3.7	0.27	16.7
Q	15	S0	1.2	0.14	10.4

^a See discussion section.

^b Films cured 3 hours at 100°C, 2 hours at 200°C, 24 hours at 300°C.

^c Film pretreatments: U - untreated, S = soaked in deionized water overnight (0), 3 days (3), and 6 days (6).

Table 3

First Hour Water and KCl Fluxes and A/B Ratios of Intrinsic Permeabilities^a
Through PMDA-DAB (I) and BTDA-DAB (II) Membranes

<u>Film^b</u>	<u>Thickness μ</u>	<u>H₂O Flux μg/cm²/sec</u>	<u>KCl Flux x 10³ μg/cm²/sec</u>	<u>A/B^a</u>
IW	2.5	6.3	1.5	5.12
IU	2.5	7.2	5.4	1.63
IIV	5	1.1	0.5	2.68

^a See discussion section.

^b Cured 3 hours at 100°C, 2 hours at 200°C, 24 hours at 300°C, and presoaked overnight in deionized water.

Table 4
Water and Urea Fluxes and A/B Ratio of Intrinsic Permeabilities^a
Through PMDA-DAB (I) and BTDA-DAB (II) Membranes

<u>Film</u>	<u>Thickness μ</u>	<u>Cure^b, and Treatment^c</u>	<u>H₂O Flux μg/cm²/sec</u>	<u>Urea Flux μg/cm²/sec</u>	<u>A/B^a</u>
IC (1 hr.)	18	1 SU	1.4		
(19 hrs.)			0.8	0.028	0.070
IZ (1 hr.)	10	2 U	1.1	0.061	0.044
(2 hrs.)			1.7	0.046	0.091
(4 hrs.)			1.7	0.038	0.110
(8 hrs.)			1.0	0.038	0.065
(48 hrs.)			0.3	0.013	0.057
IIY (1 hr.)	8	3 S	0.7		
(28 hrs.)			0.3	0.00028	2.63

^a See discussion section.

^b Film cure times and temperatures: 1 = 3 hours at 100°C, 2 hours at 200°C, 24 hours at 300°C, 2 = cured 1/2 hour at 100°C, 1/2 hour at 150°C, stripped from glass plate, Soxhlet extracted overnight with water, and cured further 15 hours at 300°C, 3 = same as 1 except 48 hours at 300°C.

^c Film pretreatment: U = untreated, S = soaked overnight in deionized water, SU = soaked overnight in 3% urea.

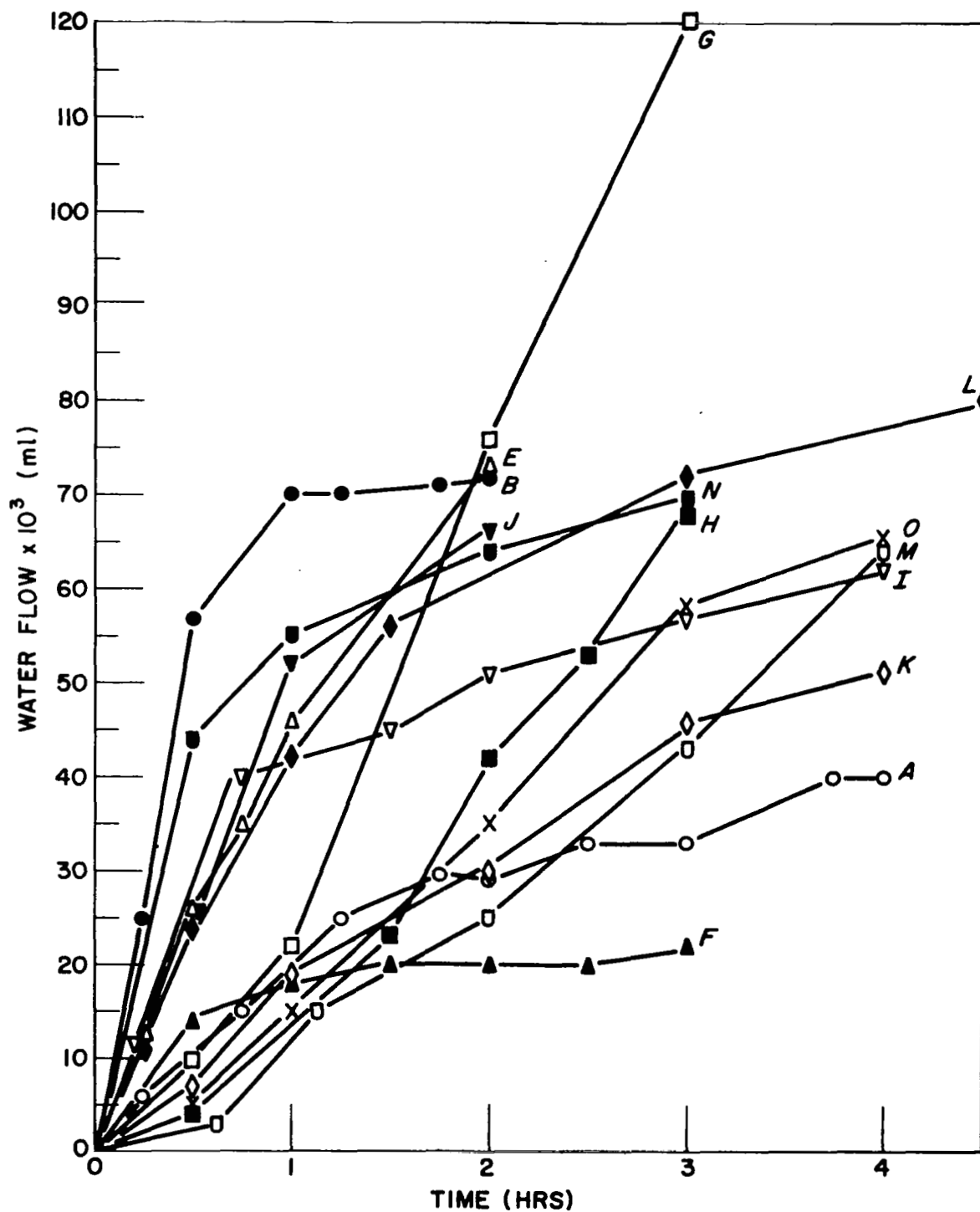


Figure 3. Initial Water Flows Through Various PMDA-DAB Membranes

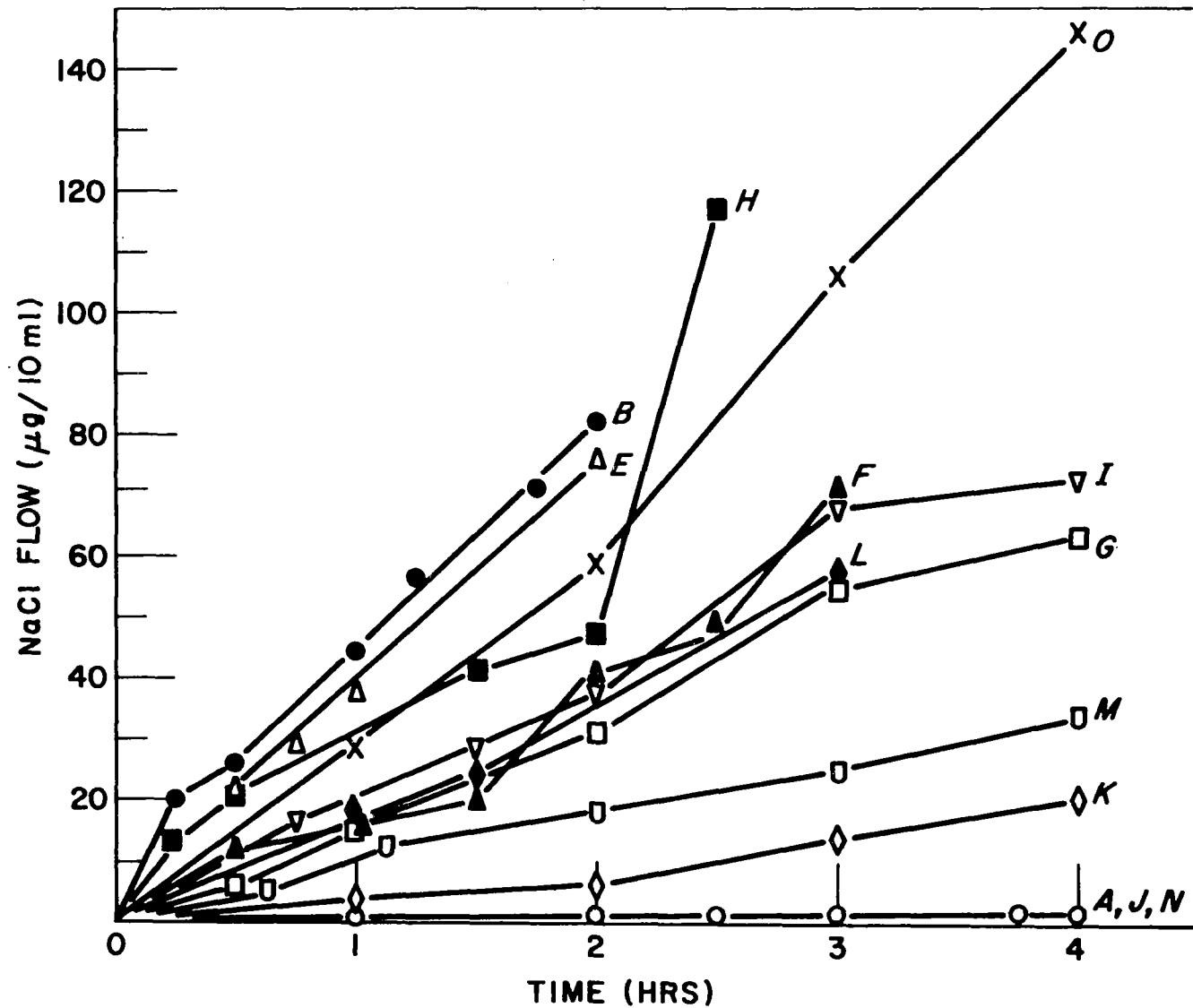


Figure 4. Initial NaCl Flows Through Various PMDA-DAB Membranes

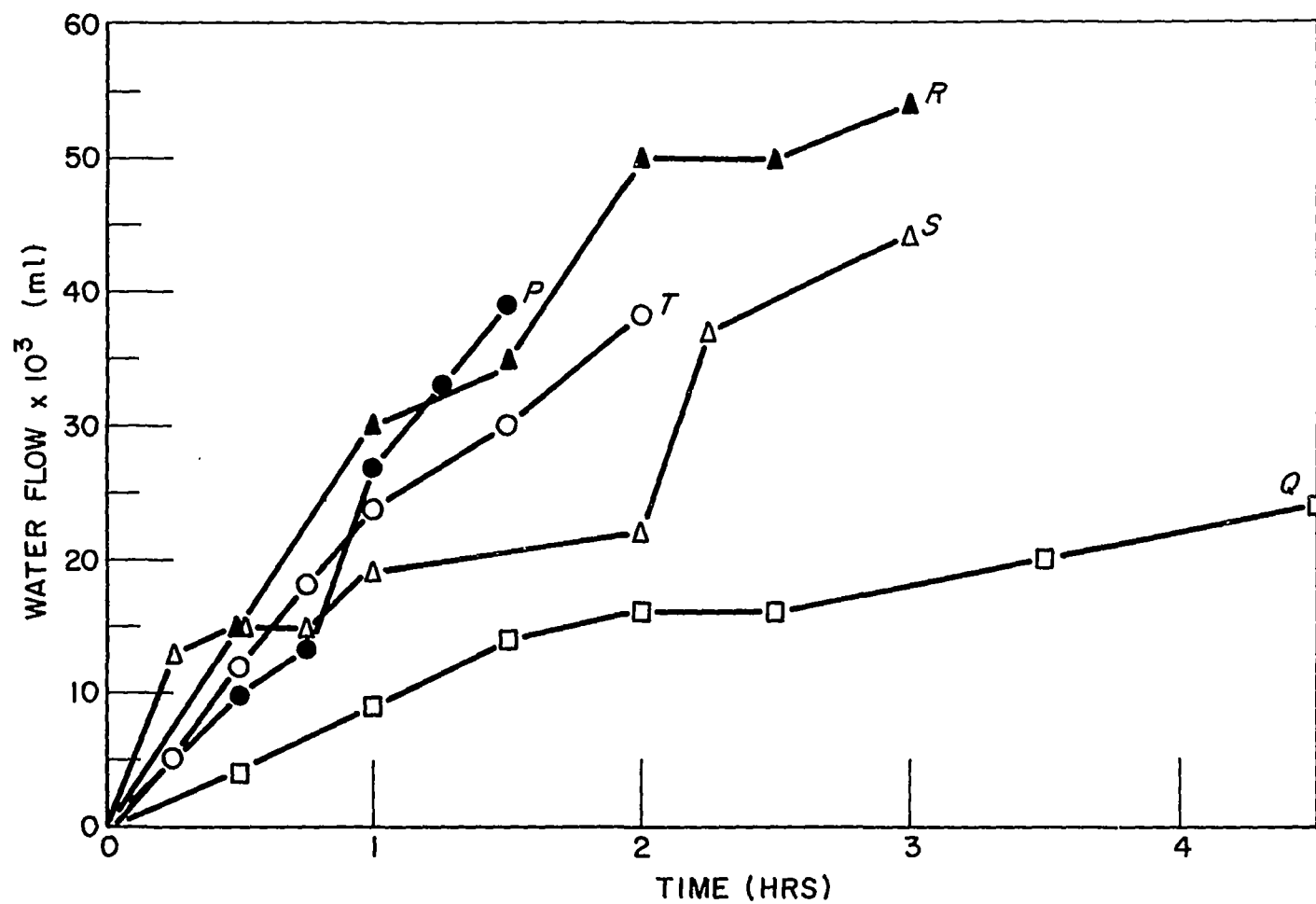


Figure 5. Initial Water Flows Through Various BTDA-DAB Membranes

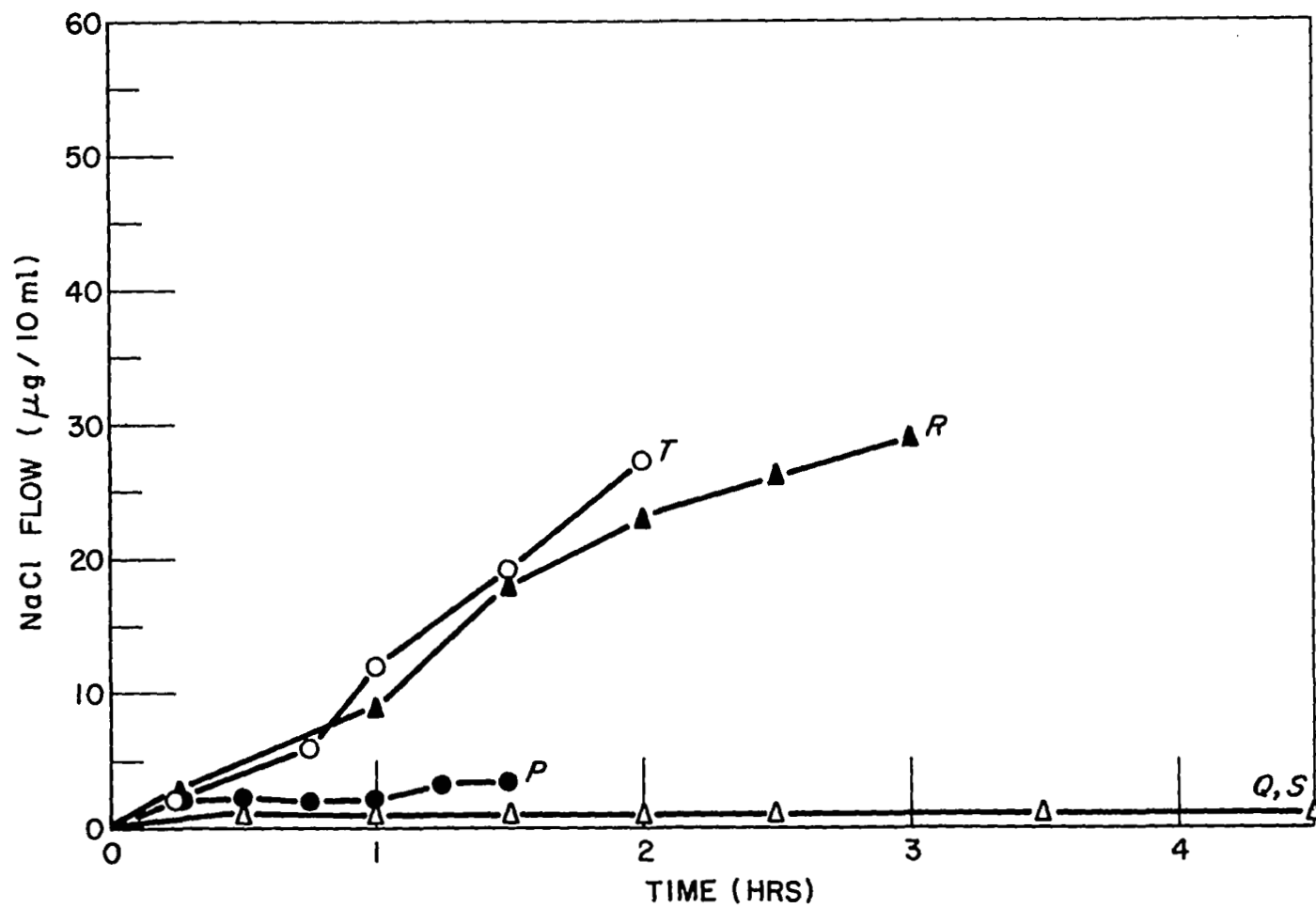


Figure 6. Initial NaCl Flows Through Various BTDA-DAB Membranes

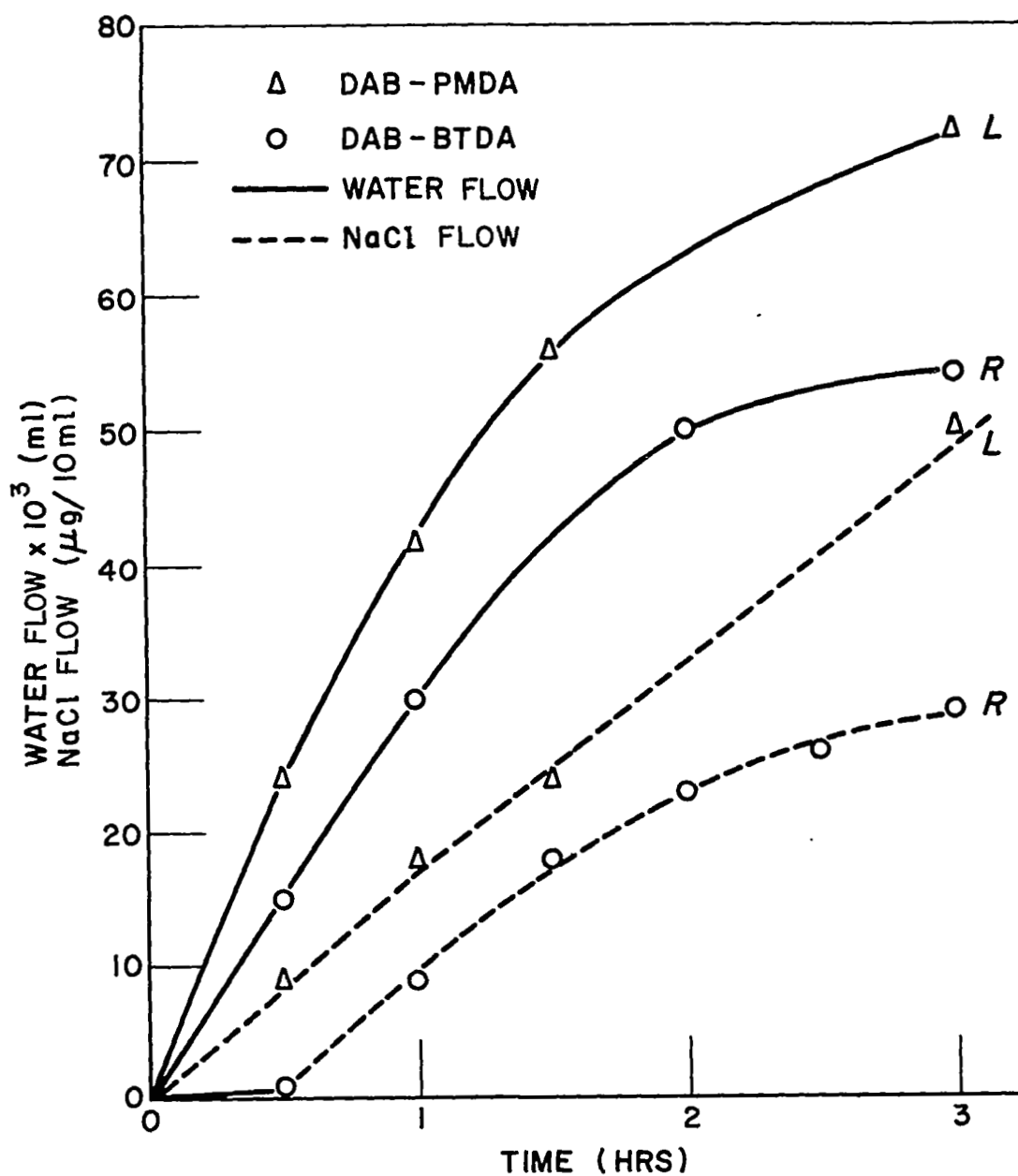


Figure 7. Initial Water and NaCl Flows Through PMDA-DAB and BTDA-DAB Membranes

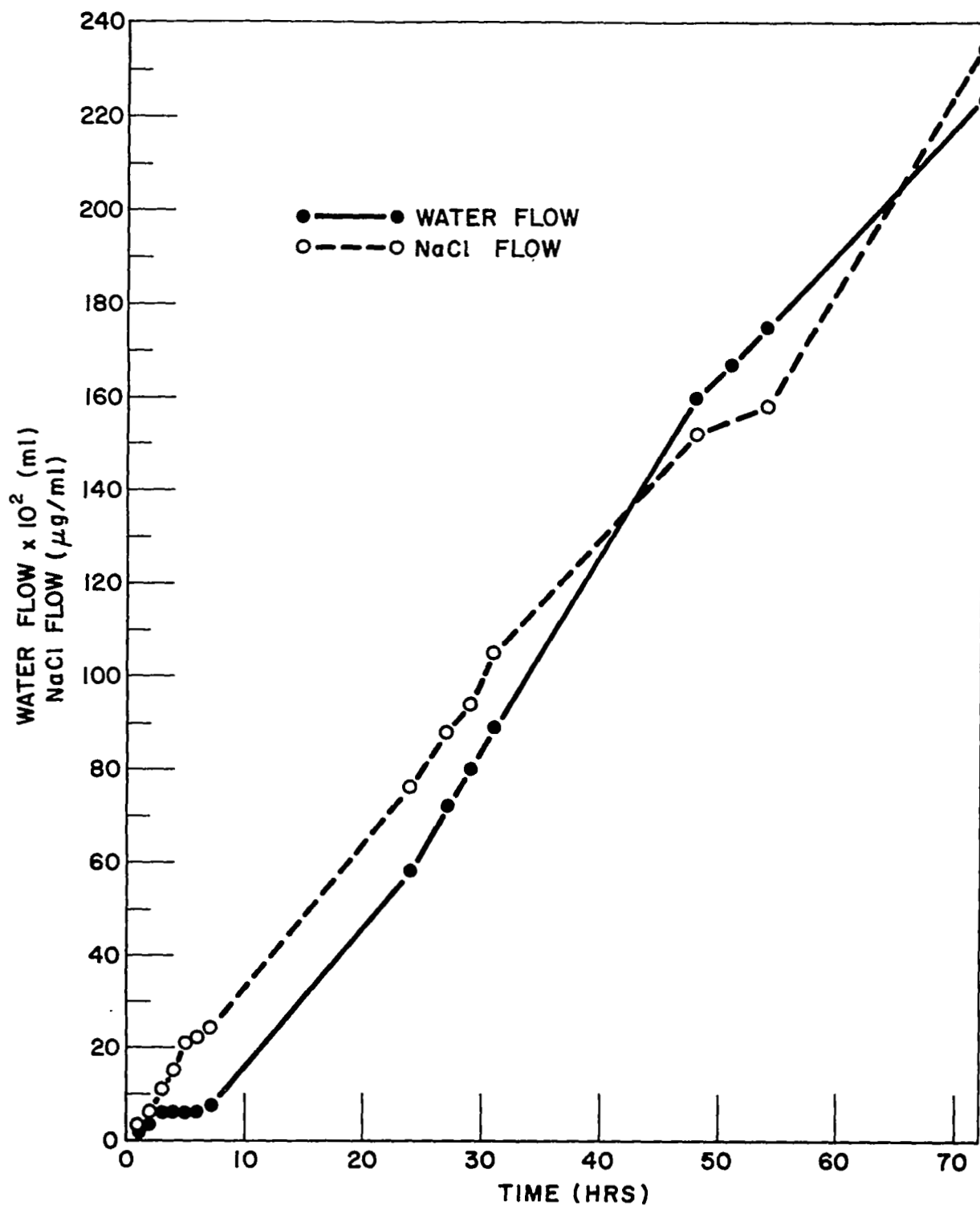


Figure 8. Extended Water and NaCl Flows Through PMDA-DAB Membrane 0

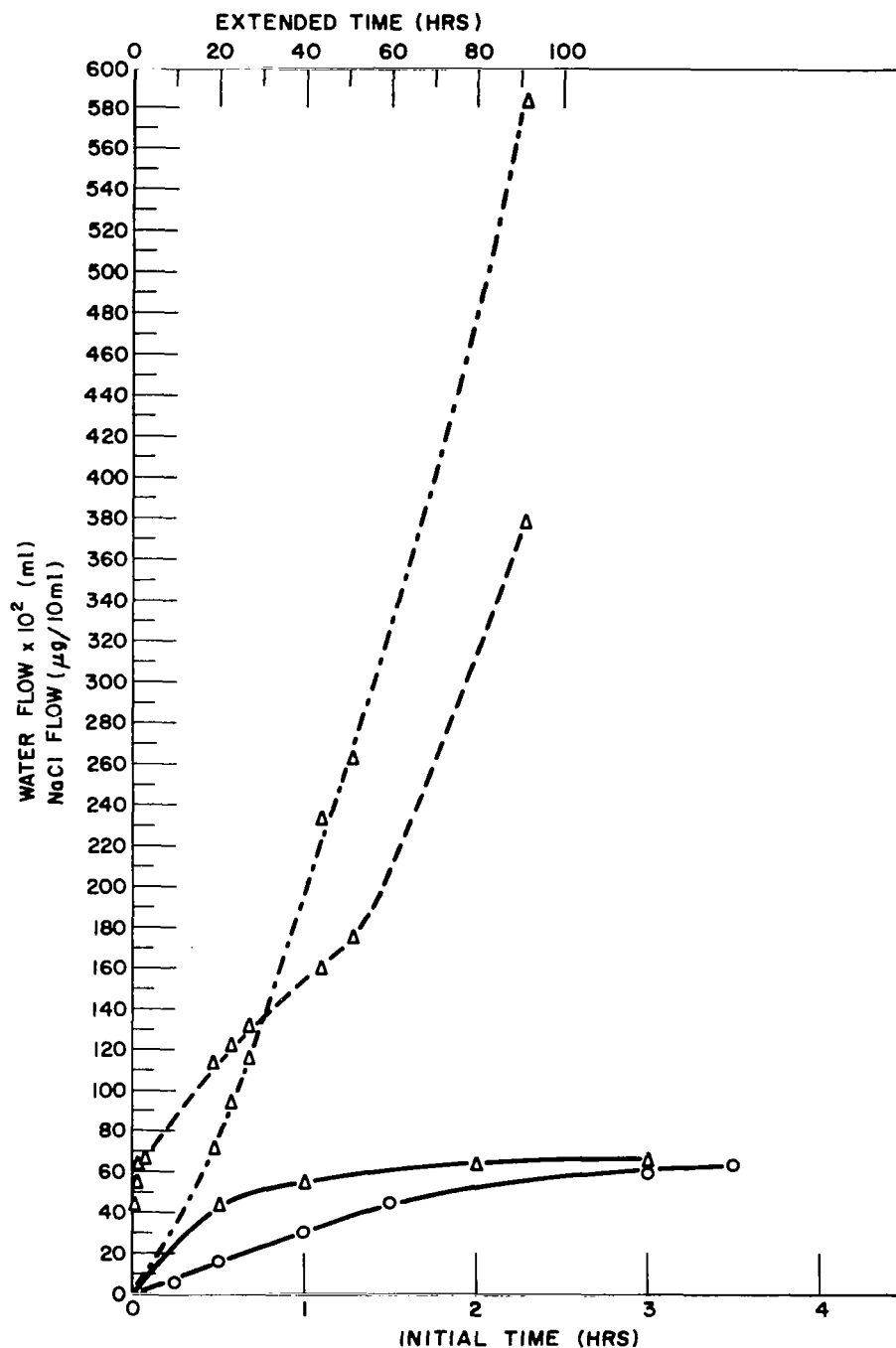


Figure 9. Initial Water Flow Through Soxhlet Extracted 2.5μ PMDA-DAB Membrane N(0—0), and, Following Replacement of Saline and Deionized Water by Fresh Solutions, Initial Water Flow (Δ—Δ), Extended Water (Δ—Δ) and NaCl (Δ—Δ) Flows Through the Same Membrane

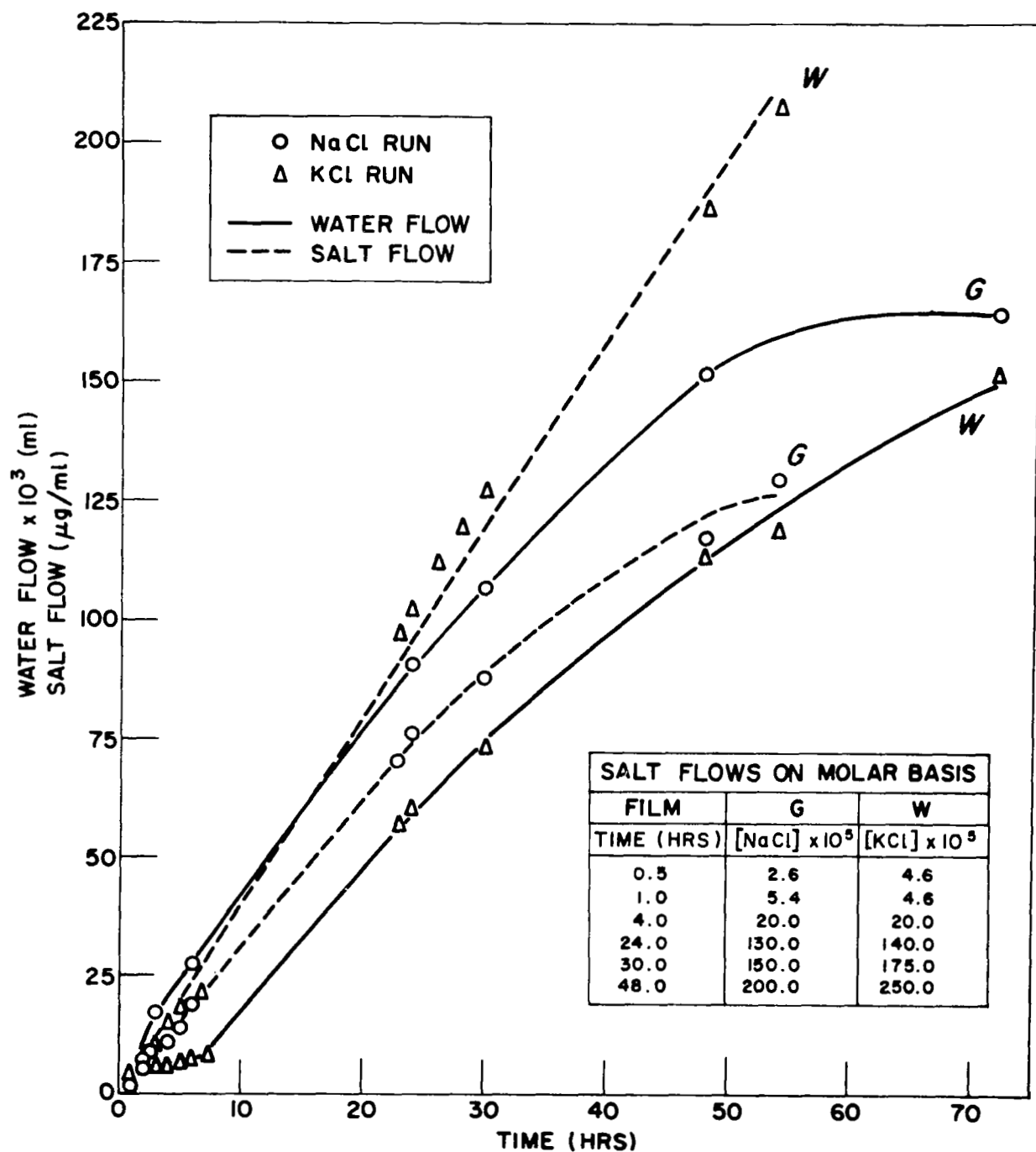


Figure 10. Extended Water and Salt Flows Through 2.5 μ PMDA-DAB Membranes

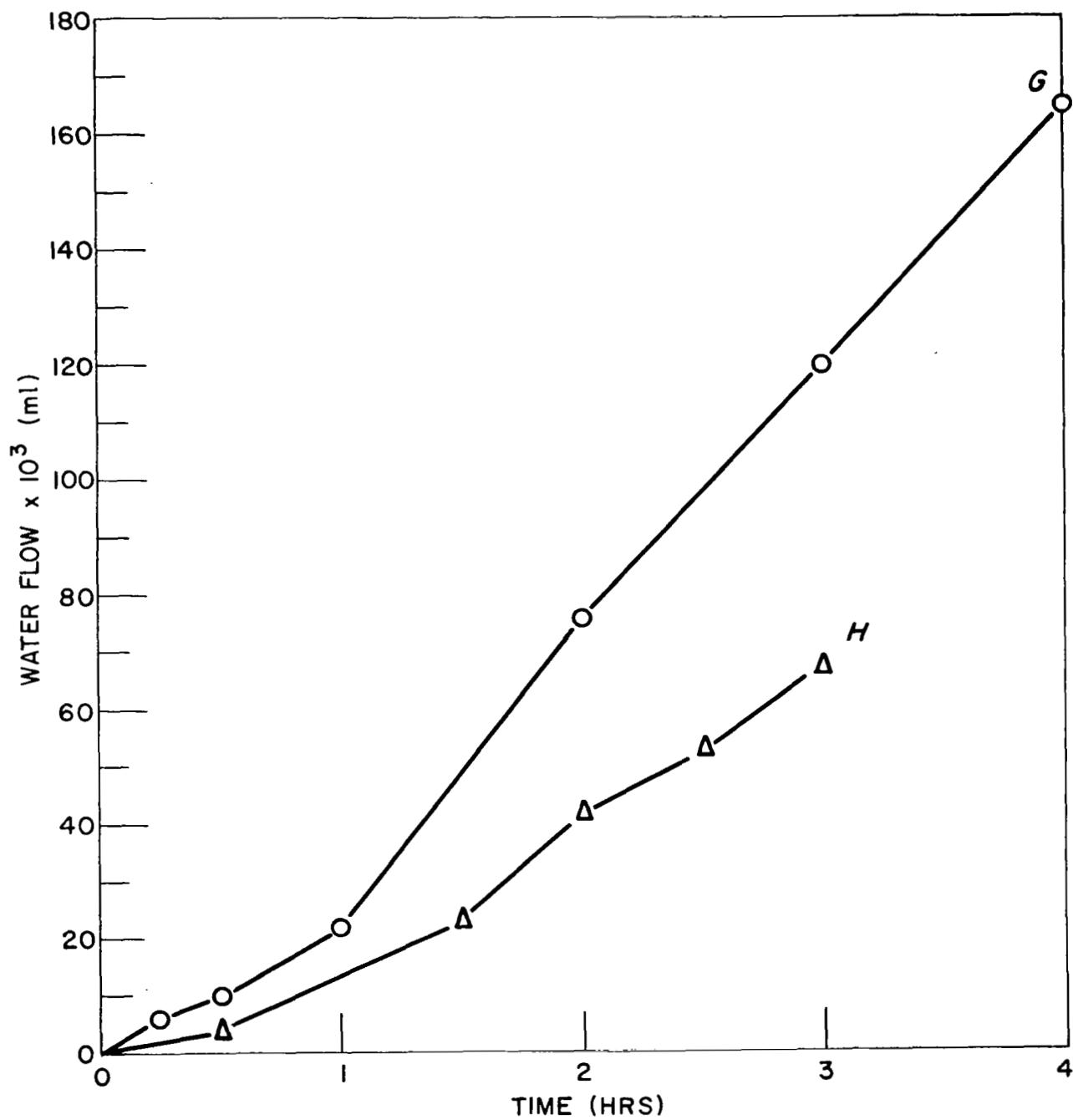


FIG. II INITIAL WATER FLOWS THROUGH 2.5 μ (G) AND 8 μ (H)
PMDA - DAB MEMBRANES

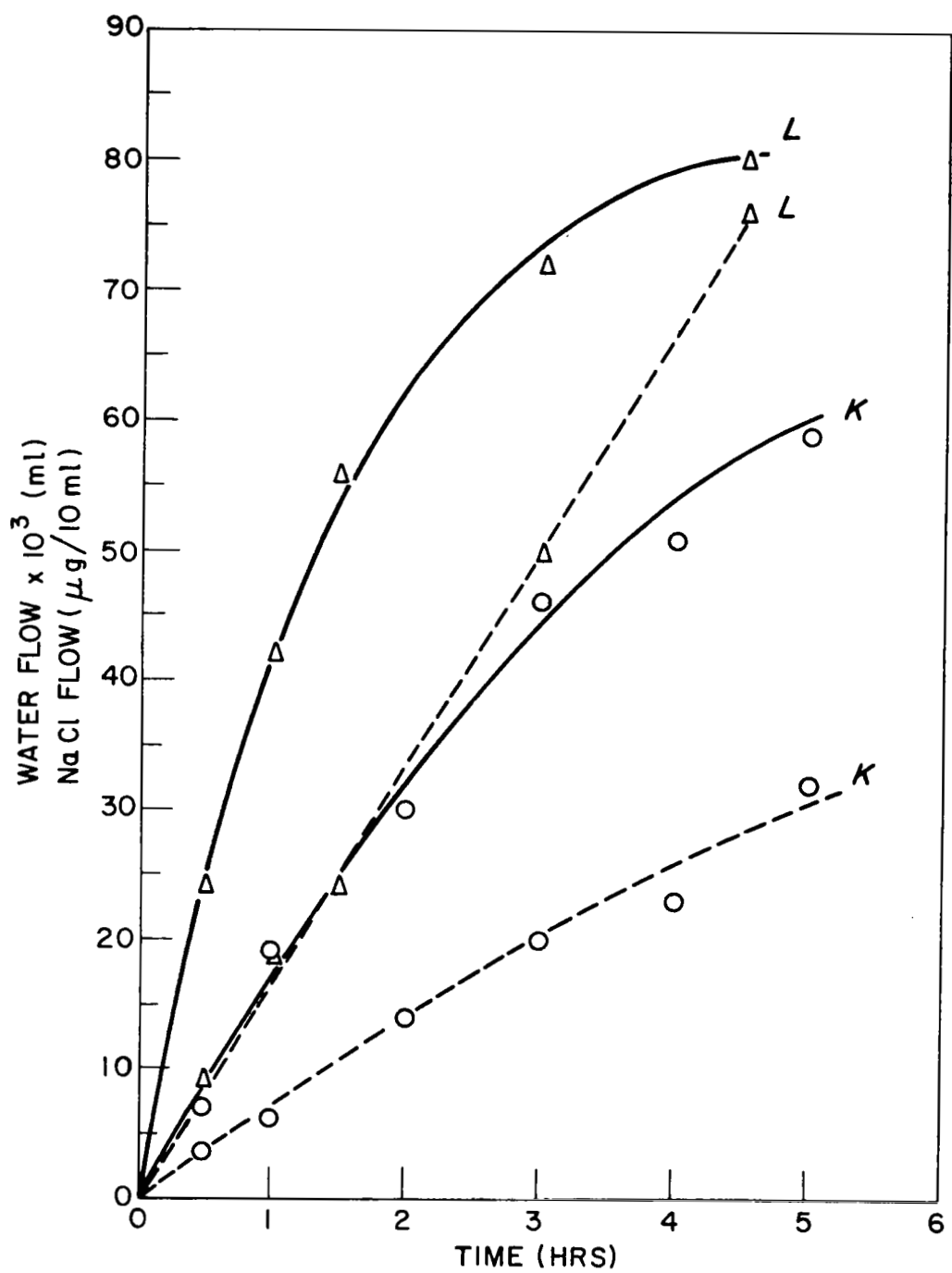


Figure 12. Initial Water (—) and NaCl (---) Flows Through Untreated (O) and Water-Presoaked (Δ) 8μ PMDA-DAB Membranes K and L

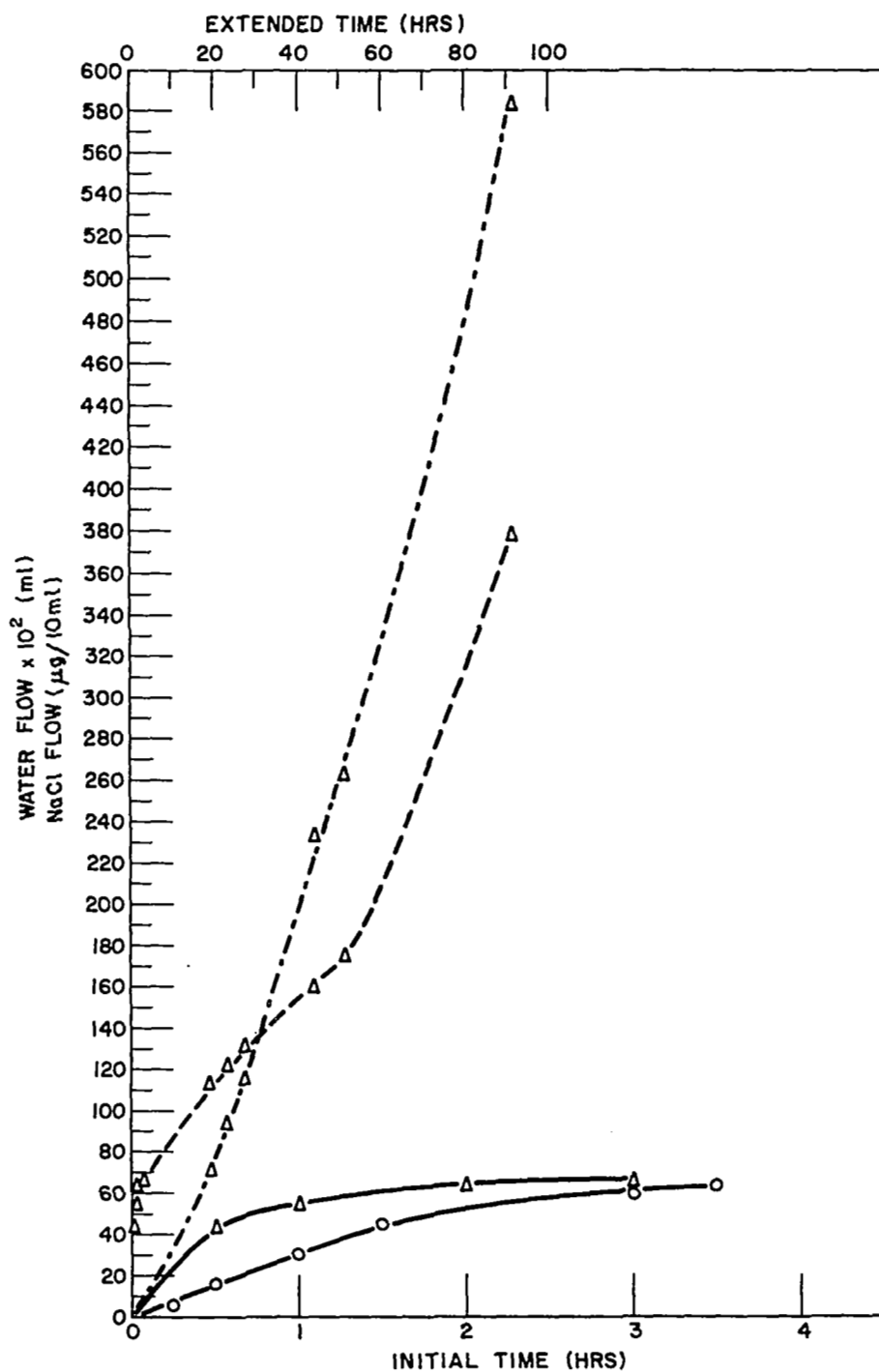


Figure 9. Initial Water Flow Through Soxhlet Extracted 2.5 μ PMDA-DAB Membrane N(0—0), and, Following Replacement of Saline and Deionized Water by Fresh Solutions, Initial Water Flow (Δ — Δ), Extended Water (Δ — Δ) and NaCl (Δ — Δ) Flows Through the Same Membrane

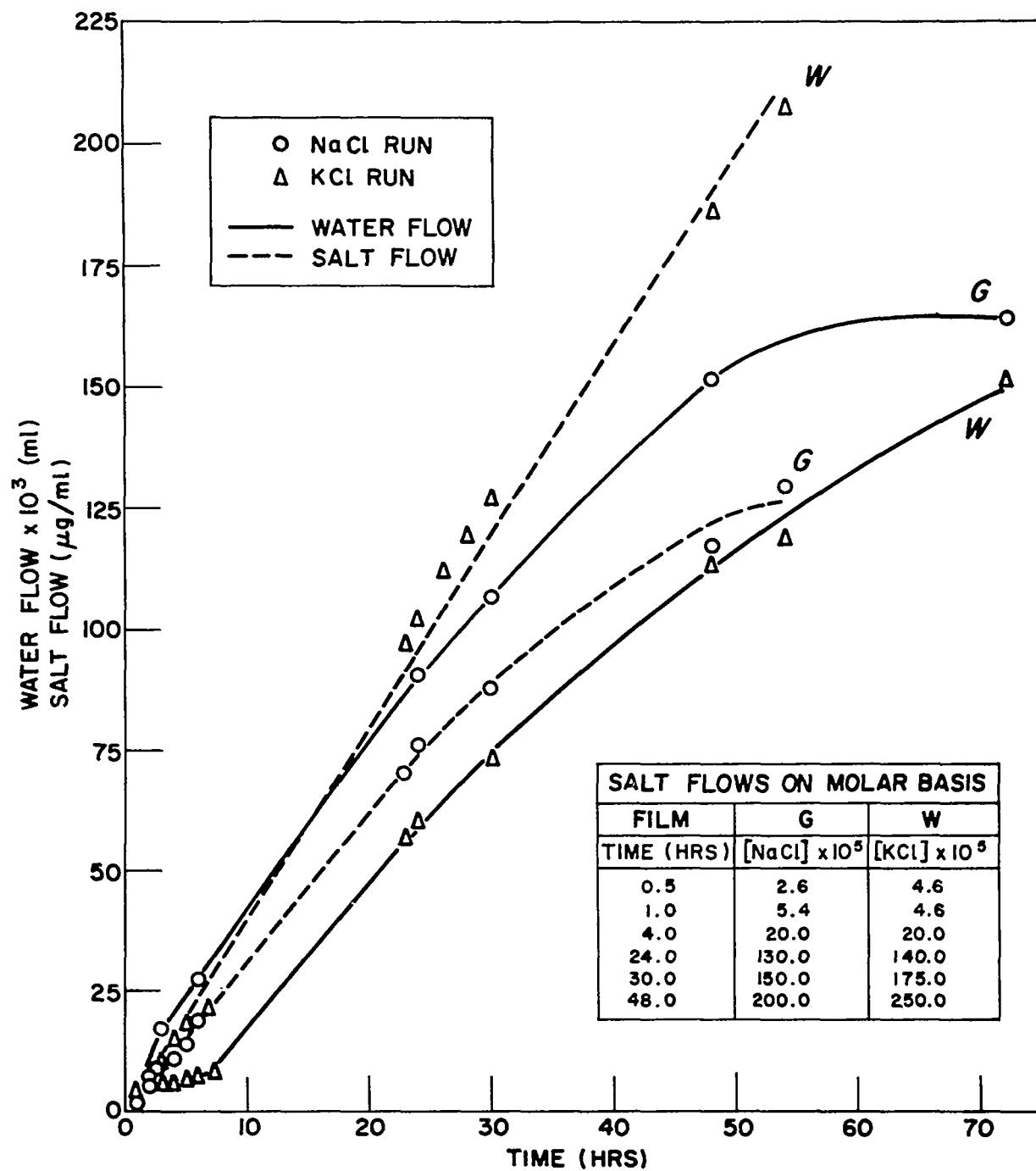


Figure 10. Extended Water and Salt Flows Through 2.5 μ PMDA-DAB Membranes

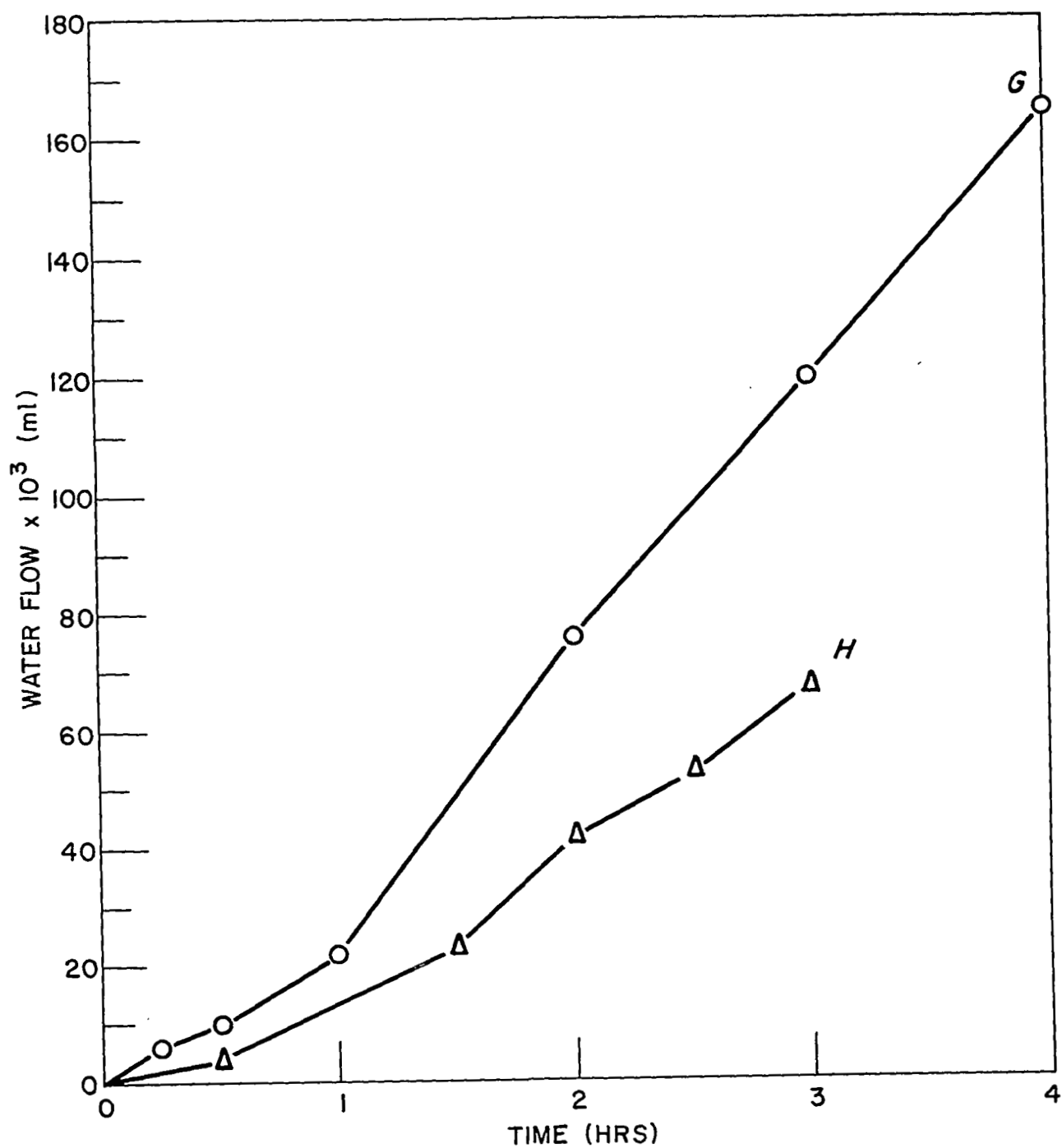


FIG. II INITIAL WATER FLOWS THROUGH 2.5 μ (G) AND 8 μ (H)
PMDA - DAB MEMBRANES

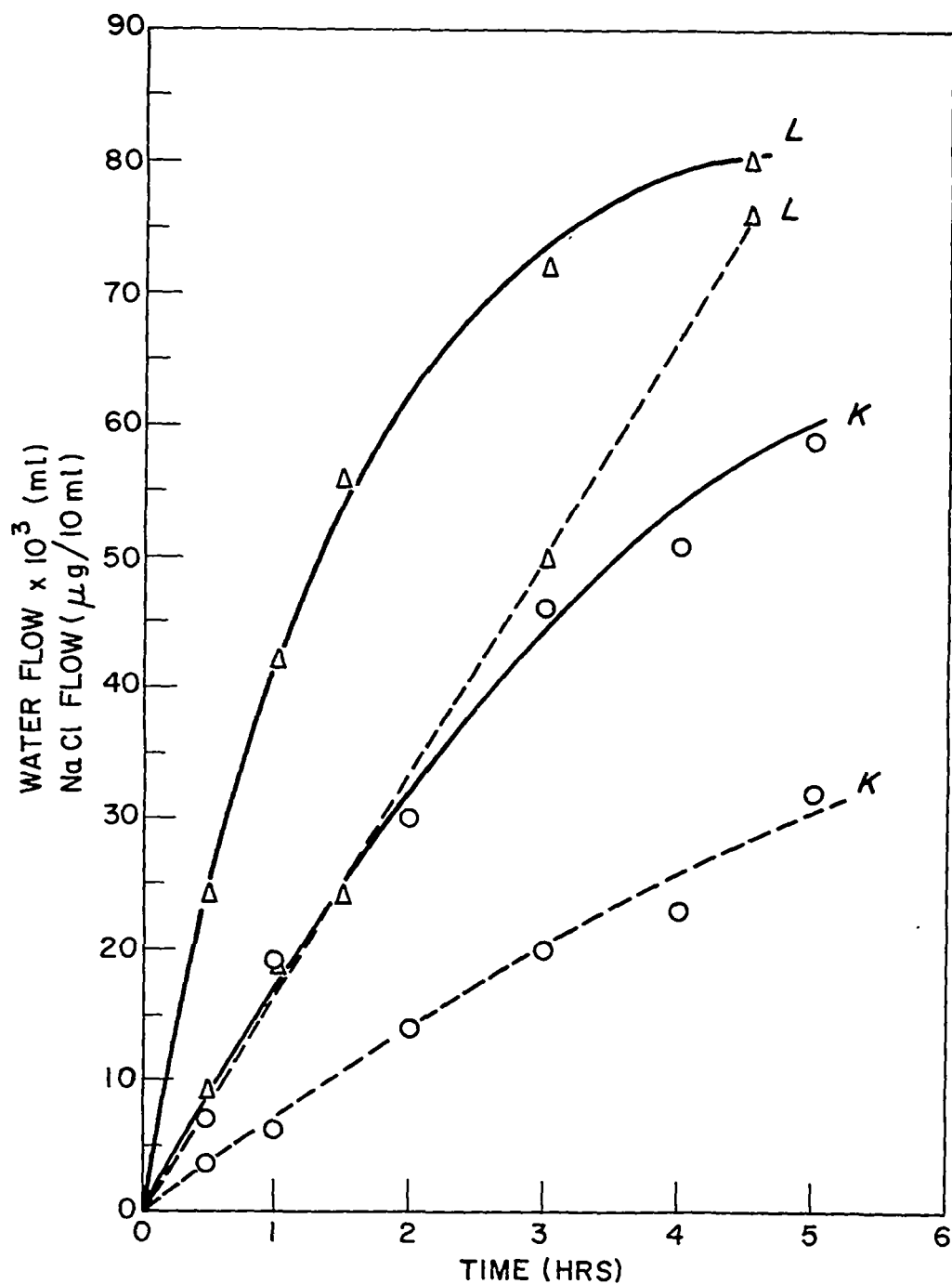


Figure 12. Initial Water (—) and NaCl (---) Flows Through Untreated (O) and Water-Presoaked (Δ) 8μ PMDA-DAB Membranes K and L

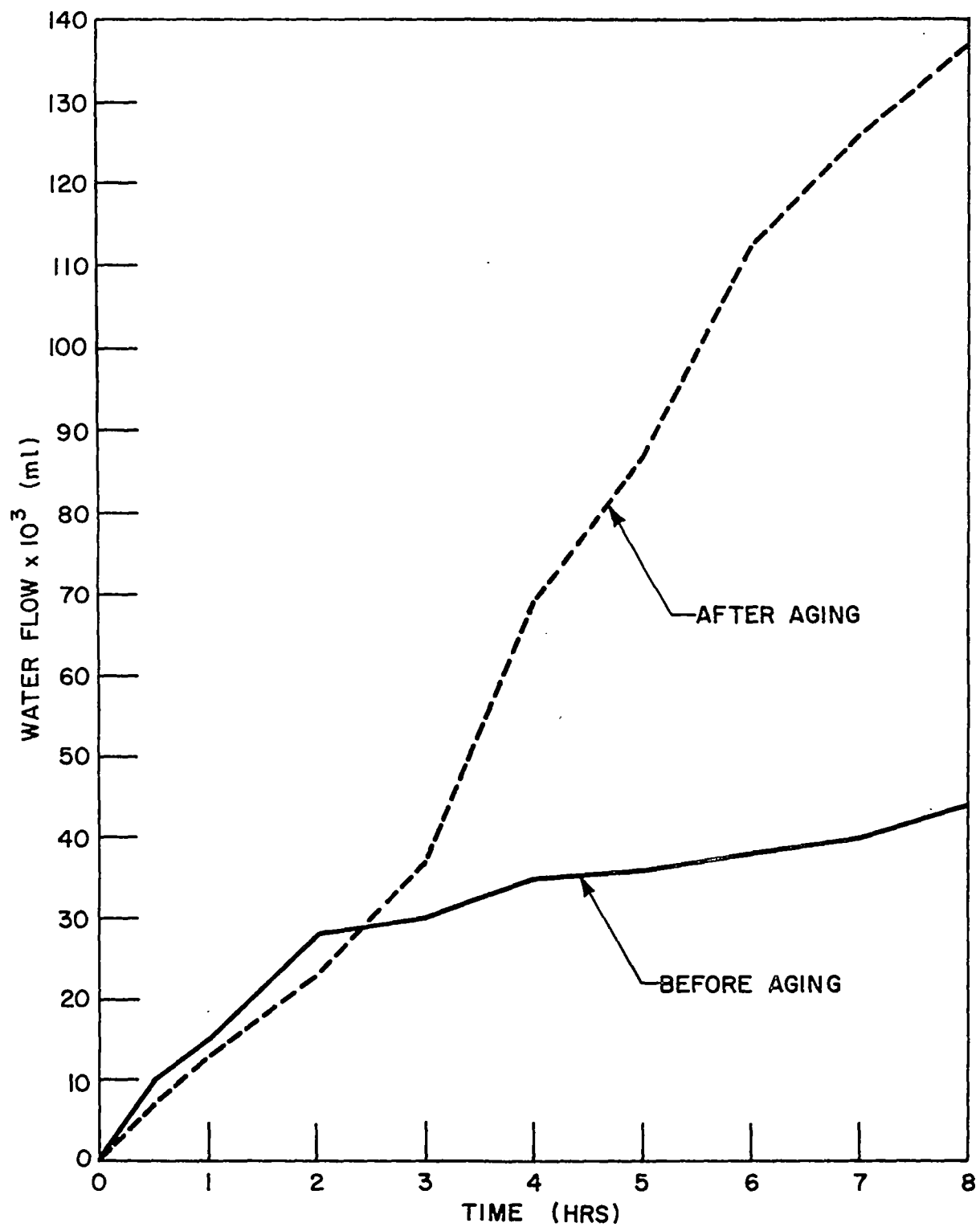


Figure 13. Water Flow Through Membrane X Before and After 30 Day Aging in Urine

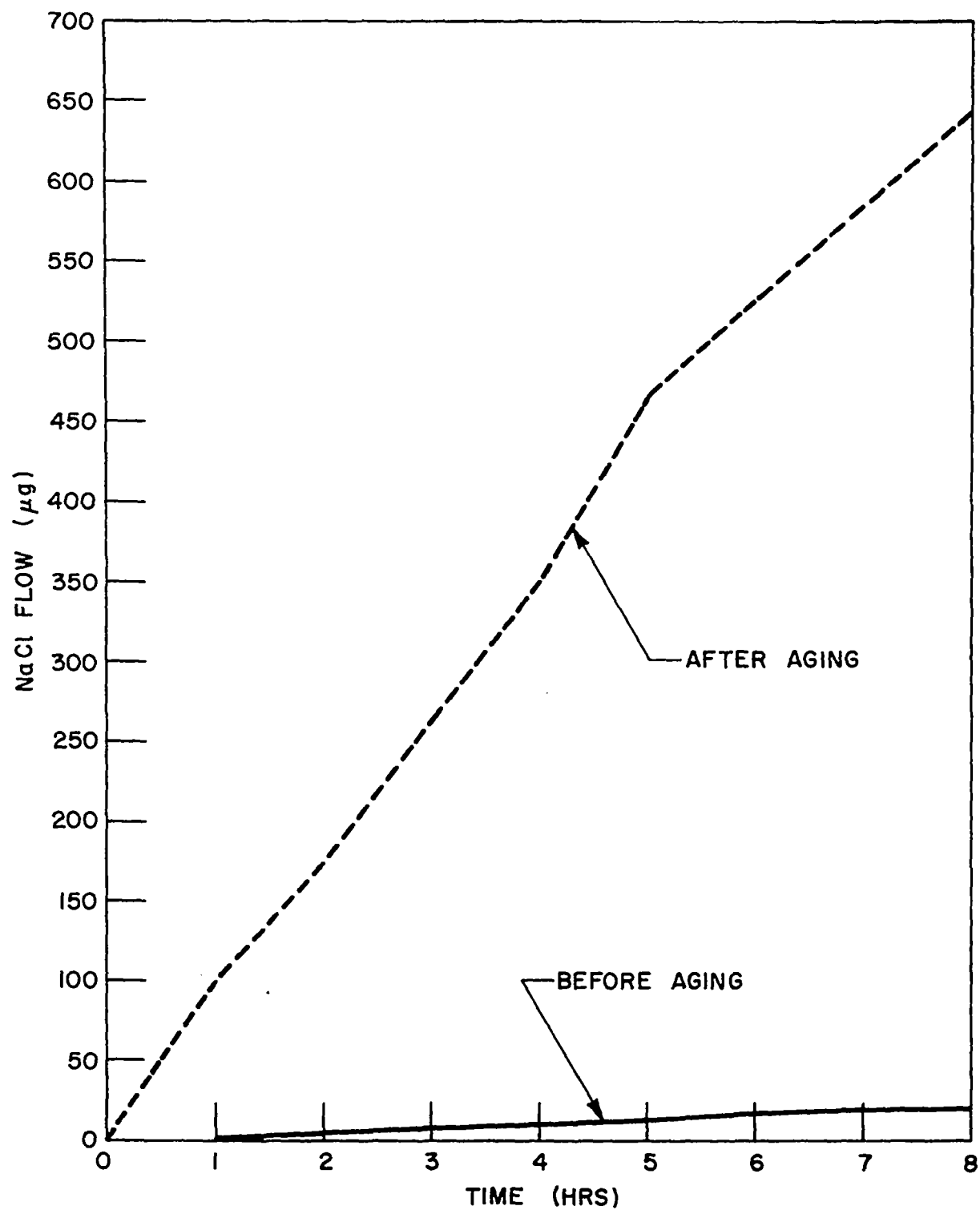


Figure 14. NaCl Flow Through Membrane X Before and After 30 Day Aging in Urine

4. DISCUSSION

4.1 Background

The four main types of processes which have been studied extensively for the economical removal of impurities from water are:

- a. Distillation (organics and inorganics)
- b. Reverse Osmosis (organics and inorganics)
- c. Ultrafiltration (microorganisms and particulates)
- d. Electrodialysis (inorganics)

Reverse osmosis is presently considered competitive in cost with distillation processes for applications other than the largest seawater desalination plants (references 7,8) even with the mechanical and chemical deficiencies of cellulose acetate membranes indicated below (reference 8). Moreover, they may also become the most economical approach to seawater purification once *durable* membranes with suitably high water and low solute permeabilities become available.

Development of reverse osmosis systems has been largely based on cellulose acetate membranes in view of their hitherto unique high water and low salt permeability characteristics (reference 9). Large scale application of these membranes, however, has been handicapped by their compressibility, low wet strength and susceptibility to hydrolysis, oxidation and microbial degradation. Moreover, the porous mechanical support (Figure 15) needed for these films is a physical obstacle obstructing the flow of water which is retarded further with time by compression of the membrane against the support. These problems are being overcome to some extent in recent years by using tubular membranes or bundles of millions of very fine hollow fibrous membranes (reference 8). In the latter case stronger and more stable polymers such as Nylon with less favorable permeability characteristics can be used in view of large active membrane surface available with this configuration (reference 8).

The characteristics and applications of cellulose acetate membranes are discussed in detail in several recent reviews (reference 7-9). Also, critical membrane parameters and relationships of intrinsic water (A) and salt (B) permeabilities to the performance of membranes in desalination applications are summarized in two recent reports from the Office of Saline Water (references 5,10).

Assuming a model based on independent water and salt diffusion mechanisms, which works reasonably well for cellulose acetate membranes (references 5,9,10), approximate values for the intrinsic water and salt permeabilities, A and B, may be obtained experimentally from respective water and salt fluxes through a membrane by using the following expressions (reference 5).

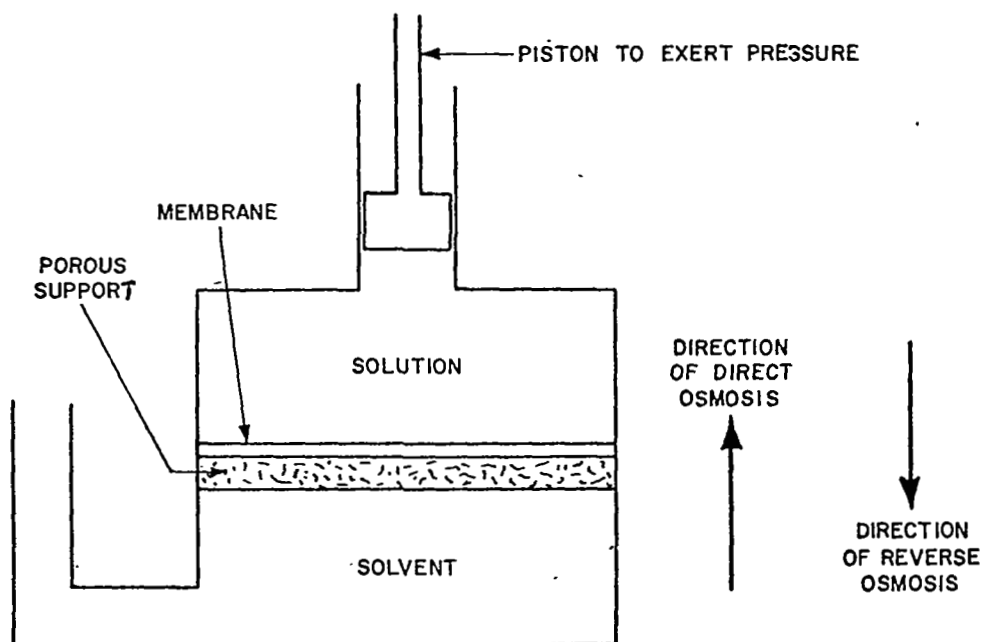


Figure 15. Schematic Diagram of Osmotic Apparatus

$$J_1 = A [\Delta P - \Delta \pi]$$

and

$$J_2 = B \Delta C, \text{ where}$$

J_1 = water flux in g/cm²/sec

J_2 = salt flux in g/cm²/sec

$$A = \text{intrinsic water permeability in g/cm}^2/\text{sec/atm} = \frac{D_1 C_1 \bar{V}_1^*}{RT\lambda}$$

ΔP = applied pressure difference across membrane in atm

$\Delta \pi$ = osmotic pressure difference = 8.2 $\Delta C \times 100$ in atm for NaCl solutions, or
= [urea] RT for urea solutions

$$B = \text{intrinsic salt permeability in cm/sec} = \frac{D_2 K^*}{\lambda}$$

ΔC = NaCl concentration gradient across membrane in g/ml, and

$$\frac{A}{B} = \frac{J_1 \Delta C}{J_2 [\Delta P - 8.2 \Delta C \times 100]} = \text{permselectivity of membrane in g/ml/atm}$$

Thus,

- a) A and B values can be obtained from direct osmosis flux measurements when $\Delta P = 0$.
- b) The water flux increases as the applied pressure is increased beyond the osmotic pressure under reverse osmosis conditions.
- c) The water flux decreases as the osmotic pressure increases if the salt concentration is allowed to build up on the pressurized side of the membrane under reverse osmosis conditions.
- d) The salt flux is independent of applied pressure.
- e) In view of factors (b) and (d) above, the higher the A/B ratio of intrinsic water and salt permeabilities of a membrane, the more purified water can be recovered per unit pressure on the salt side of the membrane, as illustrated in Table 5.
- f) The A/B ratio can be used to evaluate and compare different membranes independently of thickness under direct and reverse osmosis conditions since

* Where D_1 = diffusion coefficient of water in the membrane in cm²/sec;
 C_1 = solubility of water in the membrane in g/ml; \bar{V} = partial molar volume of water in feed; R = gas constant in appropriate units; T = absolute temperature; λ = thickness of "active" desalination layer of membrane; D_2 = diffusion coefficient of salt in the membrane in cm²/sec; and K = distribution coefficient of salt between membrane and solution being desalinated.

Table 5

A/B Values Required for Desalination to 500 ppm^a

FeedConc.	Pressure, ΔP														
	400 psi			600 psi				800 psi				1200 psi			
	a=0.50	a=0.75	a=0.90	a=0.25	a=0.50	a=0.75	a=0.90	a=0.25	a=0.50	a=0.75	a=0.90	a=0.25	a=0.50	a=0.75	a=0.90
1500 ppm	0.114	0.20	0.50	0.0584	0.0752	0.128	0.303	0.0437	0.0556	0.0953	0.222	0.0289	0.0374	0.0633	0.143
3000	0.312	0.556	1.67	0.152	0.196	0.345	0.910	0.112	0.145	0.250	0.667	0.0735	0.0953	0.161	0.40
35,000	-	-	-	11.1	-	-	-	3.70	8.33	-	-	1.64	2.63	16.7	-

^a From reference 5, p. 30. The maximum salt content of drinkable water under Public Health Service standards is 500 ppm; a = fraction of feed desalinated to this level. The salt contents of seawater and urine are about 35,000 ppm.

A and B are both inversely proportional to film thickness; and also independently of salt gradient under direct osmosis conditions when A and B are both proportional to the salt gradient.

4.2 Pyrrones and Comparison with Other Membranes

The results obtained with the Pyrrone films show considerable variability. Unfortunately, there was too little time for a meaningful systematic investigation of the causes, e.g. whether the variability was due to differences in the molecular weight of the prepolymers, curing cycles, and/or soaking and extraction treatments. We were preoccupied at first with largely unsuccessful attempts to overcome the leveling off and actual stoppage of water flux within the first 2-6 hours of a run by preparing new membranes and giving them different cures and presoaking treatments.

Eventually, it was found that if the experiment was continued when the water flux stopped, the flux increased again at rates approaching and sometimes exceeding the original rate. An example of the latter is the increase in flux observed with film 0 (Table 1 and Figure 8). These S-shaped flux interruptions may involve water-salt-membrane saturation equilibria which could be studied in more detail by flux measurements using varying salt concentrations on both sides of the membrane.

Figures 3-14 are presented mainly to give an idea of the kind of flux properties observed. They do not offer enough information for a rigorous evaluation of the effects of various experimental conditions such as membrane thickness, different curing cycles, and film pretreatments, because few films were alike and most experimental comparisons involved more than one variable. However, there are some indications that:

1. The water and salt fluxes are roughly inversely proportional to the thickness of the membrane (Figure 11), as normally expected.
2. NaCl and KCl fluxes are similar on a molar basis (Figure 10) and generally considerably less than the water flux.
3. Curing the films for at least 12 hours at 300° and presoaking the membranes overnight in deionized water or Soxhlet extracting them with water (Table 1), as well as repeated use of the membranes (Figure 9), increased the water flux.
4. Urine aging of PMDA-DAB membrane for 30 days produced a more linear water flux with time (Figure 13), an increased salt flux, and a consequent lower A/B value. The changes, however, were still within the range of flux variations observed with different unaged PMDA-DAB membranes (Table 1) and would tend to offset one another to some extent under pressurized reverse osmosis conditions. The present results suggest therefore, that a net deleterious effect of urine aging could be kept within tolerable limits. Conceivably the aging effect could be reduced, once the effects of urea, as noted below, are understood and corrected.

5. In the urea and water flux experiments (Table 4), the water flux was generally on the low side though still within the range of those observed in the water and salt flux experiments (Tables 1 and 2) particularly if the lower osmotic pressure of 3 wt. % urea (12.4 atm) versus that of 3 wt. % NaCl (24.6 atm) is taken into account. The urea flux was higher and consequently the A/B value was lower than the salt values for PMDA-DAB membranes, but urea flux and A/B value for a BTDA-DAB membrane (Table 4) were close to those obtained with salt (Table 2). As shown later, the urea rejections indicated by these results are sufficient for BTDA-DAB and insufficient for PMDA-DAB membranes to expect high urea rejection within practical reverse osmosis applied pressure limits (up to ca. 100 atm). The bleaching and polymer extension effects of exposing PMDA-DAB membranes to urea solutions, as noted earlier, may be pertinent here. They may involve some sort of solvation or relaxation effect which, conceivably, might be reduced respectively by further crosslinking or prerelaxing the polymer molecule by including in the polymer backbone some sections which are more mobile on a molecular level.
6. BTDA-DAB films gave slightly lower water fluxes than PMDA-DAB membranes (Table 2).
7. The salt flux through Pyrrone membranes was generally more constant with time than water flux, though the latter still appears fairly constant over extended periods if the initial S-shaped interruption in the water flow is viewed as a small perturbation.

The validity of these results and conclusions derived from them need to be investigated further under more systematic and rigorous testing conditions. However, since the water versus salt flux variations generally fell in a range beyond that observed with cellulose acetate membranes, this feasibility study does indicate that the water flux through Pyrrone membranes is similar to that through cellulose acetate, and superior with respect to the A/B ratio of intrinsic water and salt permeabilities; particularly if our best results with the Pyrrones shown in Table 6 are assumed to be indicative of those obtainable in further optimization studies.

The practical advantages of a high A/B ratio shown earlier in Table 5 also become evident when applied pressures required in reverse osmosis applications to obtain high salt rejection(S) are calculated from an equation derived by Lonsdale (eq. 4.3, reference 4, p. 100). Restating his permeability expressions in terms of A/B gives

$$S = \frac{1}{1 + \frac{Bc_i''}{A(\Delta P - \Delta \pi)}}$$

Assuming c_i'' (g. water/ml desalinated solution) = 1, ΔP = two applied pressures in atm. as indicated below, $\Delta \pi$ (osmotic pressure of 3 wt. % NaCl. solution) \approx 20 atm, and inserting A/B = 1 for cellulose acetate membranes and A/B = 100 for Pyrrone membranes, it is seen in Table 7 that less applied pressure is required to obtain any particular salt rejection with Pyrrones.

Table 6

Comparison of Pyrrones With Other Membranes Under Direct Osmosis Conditions

<u>Film</u>	<u>Thickness</u> <u>μ</u>	<u>H₂O Flux</u> <u>μg/cm²/sec</u>	<u>NaCl Flux</u> <u>μg/cm²/sec</u>	<u>A/B</u>
PMDA-DAB	13	7.5	0.00008	114
CA 33.6 ^a	28	19	0.80	0.0290
	23	19	0.79	0.0293
CA 37.6 ^a	19	9.0	0.044	0.249
CA 39.5 ^a	20	3.3	0.044	0.0914
	13	6.3	0.017	0.453
	15	5.4	0.074	0.0890
CA 39.8 ^a	28	2.7	0.0053	0.621
	29	2.5	0.012	0.254
	51	1.1	0.018	0.0743
	28	3.4	0.0046	0.902
CA 43.2 ^a	14	3.2	0.0079	0.494
Kapton H ^b	10	1×10^{-5}	2×10^{-8}	

^a CA = symmetric cellulose acetate film. Number = wt % acetyl content. Flux data taken from reference 10, p. 1343. It was difficult to make an experimental comparison because we used unsupported Pyrrone films, whereas weaker thin CA membranes require porous support. Available high flux asymmetric CA membranes, e.g. from Eastman Kodak's kit, are ca. 100μ thick and needed no support. Water flux was ca. 500 μg/cm²/sec with this membrane.

^b Fluxes were negligible and too small to measure accurately in two attempts.

Table 7

Calculated Salt Rejection(s) of Cellulose Acetate and
Pyrrone Membranes at Various Applied Pressures (ΔP)

<u>ΔP (atm)</u>	<u>% S for Cellulose Acetate</u>	<u>% S for Pyrrone</u>
21	50	99.0099
120	99.0099	99.9900

The salt rejection is defined as the fraction of salt in the feed held back by the membrane per unit volume of water going through the membrane, per unit membrane area, per unit time. The salt flux is unaffected by applied pressure as discussed earlier. Thus, the low salt rejection of cellulose acetate at 21 atm applied pressure, i.e. 1 atm over the counteracting osmotic pressure, reflects low water flux rather than a change in salt flux at that pressure. However, because the salt flux through Pyrrones is lower to begin with, the salt rejection with a Pyrrone membrane reaches 99% even at this low pressure.

The A/B values obtained from the urea and water flux results for PMDA-DAB membranes were lower than those derived from salt and water fluxes (Table 4). Consequently, on inserting $\Delta\pi = [\text{urea}] RT$ and the average of the low A/B values (0.073) into the equation for S above, the applied pressure required for > 99% urea rejection as noted below is too high for practical reverse osmosis application.

<u>ΔP (atm)</u>	<u>% S (urea with PMDA-DAB)</u>
1010	99.86
1510	99.91

However, inserting A/B = 2.63 for urea with a BTDA-DAB membrane (Table 4) into the equation for S above, gives high urea rejection within the practical pressure limit of about 100 atm.

<u>ΔP (atm)</u>	<u>% S (urea with BTDA-DAB)</u>
11	72.45
110	99.62

Another feature of high salt rejection is that small incremental improvements in the 99-100% salt rejection range lead to major improvements in the fraction of feed that can be recovered as desalinated water. Table 8, taken from report 255 prepared by the Office of Saline Water (reference 5, p. 21), shows calculated salt rejections (SR_f^*) required to recover certain fractions (a) as desalinated water from various feeds. The results for the 35000 ppm feed are particularly interesting because such solute concentrations are found in urine and seawater.

These evaluations of the ultimate applicability of Pyrrone membranes and comparisons with cellulose acetate membranes are based on intrinsic membrane water and solute permeability properties obtained with symmetric simple solution cast films of Pyrrones and cellulose acetate. However, more porous and water permeable asymmetric cellulose acetate membranes have been developed and used in most recent desalination studies. This development is useful in view of the previously discussed observation that applied pressure enhances the water flux more than salt flux. Such modified or asymmetric cellulose acetate membranes, first developed by Loeb and Sourirajan, are made by various solution casting techniques (Loeb, Chapter 3, reference 9). They consist of a relatively thick, ca. 100 μ spongy membrane with a hard skin similar to conventionally cast film which serves as the principal salt barrier. The water flux properties of these asymmetric membranes are about 100-1000 times better than those of thinner conventional symmetric membranes.

It seems reasonable to believe that Pyrrone membranes could be physically modified in a similar manner by developing appropriate film forming procedures. The more favorable properties of the Pyrrones such as compressive strength, chemical durability, and A/B ratio of intrinsic water and salt permeabilities, could then be exploited in several ways to yield more durability and/or greater water to salt fluxes than can be obtained with cellulose acetate. For instance, the better A/B ratio itself would enhance the water to salt flux and salt rejection under pressure, and this could be maintained longer or increased further by higher pressures than can be used with asymmetric cellulose acetate membranes in view of higher compressive strength of the Pyrrones. Or, the water flux, salt rejection, and desalinated water recovery could be further increased by using Pyrrones that are more porous and permeable to water than asymmetric cellulose acetate membranes and yet could withstand similar pressures in view of better strength.

We believe, therefore, that the practical significance of the observed Pyrrone flux properties is as follows.

5. CONCLUSION

Comparable water flux and superior intrinsic water to salt permeability properties of Pyrrone versus symmetric cellulose acetate membranes, coupled with better strength and chemical resistance, suggest that asymmetrically

* $SR_f(\text{inal})$ = Salt rejection required at the "final stage" of recovering a feed fraction (a) as desalinated water. $SR_f \approx SR_i(\text{nitial})$ for high salt rejection membranes.

Table 8

% SR_f as a Function of the % Water Recovery, $a \times 100$, at
Different Feed Concentration

For 35000 ppm \rightarrow 500 ppm

a = 0	% SR_f = 98.6
0.25	99.0
0.50	99.4
0.75	99.7
0.90	99.9

For 3000 ppm \rightarrow 500 ppm

a = 0	% SR_f = 83.3
0.25	87.0
0.50	90.9
0.75	95.3
0.90	98.0

For 1500 ppm \rightarrow 500 ppm

a = 0	% SR_f = 66.7
0.25	72.8
0.50	80.3
0.75	88.9
0.90	95.2

modified Pyrrone membranes, if they could be prepared, may outperform the best reverse osmosis membrane developed to date, i.e., the asymmetrically modified cellulose acetate membrane.

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